

# PATENT SPECIFICATION

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## (54) ADHESIVE COMPOSITION

(71) We, KURARAY CO. LTD., a body corporate organized and existing under the laws of Japan, of 1621, Sakazu, Kurashiki-City, Japan, ASAHI CO. LTD., a body corporate organized and existing under the laws of Japan, of 1—17 of 2 Senju-Sakuragimachi Adachi-ku Tokyo, Japan and KOYO SANGYO CO. LTD., a body corporate organized and existing under the laws of Japan, of 2—8 Kanda-Kajimachi Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention is concerned with a water-resistant adhesive that is especially useful for bonding of wood.

At present, urea resins, melamine-urea condensation resins and phenol resins are predominately used as the adhesives for making plywood. These adhesives are widely used because of their low price and relatively good water-resistance; however, it has recently been found that evaporation of residual formaldehyde (hereafter called "formalin") from the adhesive adversely effects the environment within the plywood factory and release of formalin from furniture or housing made therefrom has been found injurious to the human body.

Although several attempts have been made recently to decrease the generation of formalin, they have all been largely unsuccessful since it is impossible, in principle, to reduce the generation of formalin to essentially zero. Moreover, the fluctuations in hot pressing conditions during the process for producing plywood, can result in incomplete curing of the adhesive, giving rise to the subsequent generation of formalin. Therefore, the use of condensation resins containing formalin in the preparation of plywood has been severely restricted.

Furthermore, other adhesives which do not

contain formalin, such as protein or polyvinyl acetate based adhesives, are not useful, generally, due to their poor water resistance.

Another adhesive that has heretofore been used in plywood production and which does not contain formalin is a polyvinyl alcohol (hereafter PVA)-isocyanate system as described in United States Patent No. 2,277,083. In this United States Patent, PVA and an isocyanate are used in combination in a non-aqueous medium. For example, the procedure as set forth in Example 2 of the said patent is as follows: After coating an aqueous solution of PVA on a single board and drying, a solution of hexamethylene diisocyanate in toluene is coated over the PVA layer. By laminating several ply in this manner, plywood is manufactured. It is apparent that, in this manner, it is generally impossible to manufacture plywood with sufficient adhesive strength, as shown by a comparative example in the said patent.

Furthermore, though it is well known that related isocyanate compounds react easily with compounds having an active hydrogen, isocyanates were not previously used as a waterproofing component of an adhesive in an aqueous medium, for the reason that, not only do they decompose easily when mixed with water, generating carbon dioxide gas and resulting in a substantially unworkable system, but also no good effects are expected from the standpoint of stability and waterproofing.

The present invention provides an adhesive composition comprising (1) an aqueous solution of poly vinyl alcohol and (2) a hydrophobic solution of an isocyanate compound or polymer that contains two or more isocyanate groups to the molecule. The composition may also contain an aqueous emulsion of vinyl acetate polymer and/or an aqueous latex of butadiene polymer. The adhesives of the present invention can be prepared by uniformly dispersing a solution in a hydrophobic solvent of the said isocyanate compound or

polymer into ingredient (1) or a mixture of ingredient (1) with the aqueous emulsion of vinyl acetate polymer and/or aqueous latex of butadiene polymer. However, if the isocyanate compound or polymer without solvent, or dissolved in a solvent other than the said hydrophobic solvent herein, is dispersed in the PVA, it is impossible to get such a water-resistant adhesive.

It has been found that adhesives of the present invention exhibit superior water-resistance and an excellent initial adhesive strength (see the Examples).

In the present invention, the presence of water is important. If a solvent other than water is used for the vinyl alcohol, vinyl acetate or butadiene polymer solutions, emulsions or latices, it is impossible to get such a superior water-resistant adhesive.

In the present invention, the aqueous emulsion of a vinyl acetate polymer can be, for example, an aqueous emulsion of polyvinyl acetate or an aqueous emulsion of a copolymer of vinyl acetate and a comonomer polymerizable with it (e.g. a copolymer of vinyl acetate and ethylene).

Further, the aqueous latex of butadiene polymer can be, for example, an aqueous latex of copolymer of butadiene and styrene (SBR), an aqueous latex of copolymer of butadiene and acrylonitrile or an aqueous latex of a copolymer of butadiene and another comonomer polymerizable with it.

The concentration of solid content in the aqueous emulsion or latex preferably ranges from 10 to 80% by weight, particularly from 30 to 60% by weight.

SBR latices that can be used in this invention include commercially available SBR and modified SBR products. Use of modified SBR obtained by copolymerizing or adding a carboxyl group or carboxylic acid salt to SBR, adding a hydroxyl group to SBR latex and other modified SBR formed by adding at least one functional group selected from amide, amino, sulfonic and epoxy groups and their salts is especially preferred. By the term "latex added with a carboxyl group or carboxylic acid salt" is meant a latex in which a carboxylic group or carboxylic acid salt is contained in at least one of the latex-constituting polymer or surfactant. As the carboxylic group-containing unsaturated monomer, there may be mentioned copolymerizable unsaturated organic acids such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, partially esterified itaconic acid, maleic acid, maleic anhydride and partially esterified maleic acid. SBR in which a carboxylic acid salt (for instance, a sodium, potassium, calcium or ammonium salt) is formed by adding a basic substance to a carboxyl group containing SBR can also be used. The SBR need not necessarily contain a carboxyl group or its salt, but a carboxyl group or its salt may be contained

in a surfactant or stabilizer to be used in the polymerization process. As such a surfactant, there may be mentioned saponified products of fatty acids, namely various soaps.

By the "hydroxyl group added latex" is meant a latex in which a hydroxyl group is contained in at least one of the latex-constituting polymer or surfactant. As the hydroxyl-group-containing unsaturated monomer, there can be mentioned copolymerizable monomers such as allyl alcohol, 2-hydroxyethyl (meth) acrylate, 2-hydroxypropyl (meth)acrylate, mono-allyl ethers of polyhydric alcohols, and N-methylol (meth)acrylamide. Hydroxyl-group-containing polymer latices prepared by methods other than that mentioned above may be used. For instance, a polymer latex formed by adding a small amount of a basic substance to a copolymer containing vinyl acetate as one component and partially saponifying vinyl acetate to introduce a hydroxyl group into the copolymer can be used. The hydroxyl group need not necessarily be contained in the latex-constituting polymer, but it may be contained in a surfactant or stabilizer to be used in the polymerization process. As such surfactant, there may be mentioned, for instance, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers and oxyethylene-oxypropylene block copolymers.

By the term "the latex added with at least one functional group selected from amino, amide, sulfonic and epoxy groups and their salts" is meant a latex in which the functional group is contained in at least one of the latex-constituting polymer or surfactant. As the unsaturated monomer containing such a functional group as amino, amide, sulfonic and epoxy groups, there may be mentioned copolymerizable monomers such, for example, as glycidyl (meth)acrylate, allyl glycidyl ether, dimethyl-aminoethyl methacrylate, vinylpyridine, *t*-butylaminoethyl (meth)acrylate, acrylamide, methacrylamide and maleinamide. Latices containing a salt (for example, amine hydrochloride) formed by adding a basic substance or acidic substance to the foregoing functional group-containing polymer latices can also be used. Such functional group need not necessarily be contained in the latex-constituting polymer, but it may be contained in a surfactant or stabilizer to be used in the polymerization step. As such surfactants, there may be exemplified polyacrylamide, alkylamine sulfates, sodium monobutylphenylphenol sulfate, sodium monobutylphenylphenylphenol sulfate, sodium dibutylphenylphenol sulfate, sodium monobutylphenylphenylphenol sulfate, sodium dibutylphenylphenylphenol sulfate, sodium alkylallyl sulfonate, sodium dodecylbenzenesulfonate, sodium paraffin sulfates, sodium lauryl sulfate, sodium secondary alcohol (having 14 carbon atoms) sulfate, and sodium octyl alcohol sulfate. Namely, these surfactants contain in the

molecule a functional group such as an amide group, a sodium sulfonate or an amine salt.

Among the foregoing modified SBR latices, a carboxyl-group- or carboxylic-acid-salt-copolymerized or added latex is especially preferred. The content of the carboxyl group-containing organic acid in the latex is 0.1 to 30% by weight, preferably 0.2 to 15% by weight, based on the total solids. These latices can be prepared in an aqueous system according to customary methods with use of a radical initiator, a surfactant and an agent to adjust viscosity, conversion and rate of polymerization. In addition to the above-exemplified surfactants, various anionic, non-ionic and cationic surfactants can also be used.

It is possible to add as a protective colloid a water-soluble macromolecular substance such as mentioned above before, during or after the polymerization. The so formed aqueous latex can also be used in this invention.

The primary reason for use of SBR in this invention is that the characteristic properties of a film formed from a blend of SBR with PVA are improved to increase the normal state bonding strength of bonded wood and the water-resistance of the resulting bond. The secondary reason is that by using SBR latex added with a carboxyl group or its salt, a hydroxyl group or an amino, amide, sulfonic, isocyanate or epoxy group, the functional group in the latex is allowed to react with a compound having at least two isocyanate groups, which is incorporated in the adhesive composition, to form a water-insoluble, cross-linked net-like structure and give a bond exhibiting excellent water resistance. The third reason is that by use of such an SBR latex it is possible to increase the concentration of solids at a viscosity within such a range as will not cause any operational trouble and to obtain an adhesive composition having good coating processability and a highly improved initial bonding strength. Accordingly, use of an aqueous SBR latex is preferred in this invention.

The concentration of PVA in the aqueous solution desirably ranges from 5 to 20 weight percent. The PVA can exhibit a degree of polymerization ranging from 300 to 2500 and a degree of saponification of from 80 to 100 molar percent, and it is especially desirable to use a PVA having a high degree of saponification.

The aqueous PVA solution can be prepared using hot water, or, in the case of PVA soluble in cold water, it is possible to first mix it with an additive or filler and then dissolve it in water just before coating.

In this invention, it is preferable to have PVA present in the above described aqueous emulsions or latices. The concentration of PVA in the aqueous emulsion or latex preferably ranges from 5 to 20% by weight.

The mixing ratio of PVA (solid content) to

the aqueous emulsion or latex (solid content) preferably ranges from 5 to 2000% by weight, particularly from 10 to 1000% by weight.

In the present invention, the isocyanate compound or polymer is a molecule which has more than two isocyanate residues, such as, tolylene diisocyanate (TDI, for example that sold under the trade mark *Desmodur T* of Bayer Incorp.), hydrogenated TDI, trimethylolpropane (TMP) — TDI adduct (*Desmodur L*), triphenylmethane - triisocyanate (TTI, *Desmodur R*), methylene-bis-diphenylisocyanate (MDI, *Desmodur 44*), hydrogenated MDI, hexamethylene diisocyanate (*Desmodur N*), xylenediisocyanate and 4,4'-dicyclohexylmethanediisocyanate.

Furthermore, a mixed system of a polyisocyanate and a polyol, for example, a mixture of polyols such as polyester or polyether with hydroxy groups and an excess of isocyanate such as the said *Desmodur L*, can also be used.

Furthermore, it is possible to use a prepolymer system, such as a prepolymer with NCO end groups, partially polymerized from a polyol and an excess of polyisocyanate, or a prepolymer with OH end groups, partially polymerized from an excess of polyol, mixing it with an excess of the above mentioned *Desmodur L*, just before coating.

The mixing ratio of isocyanate compound or polymer to PVA (solid content) and/or emulsion and/or latex (solid content) in the adhesive can range from 0.1 to 200, preferably 1 to 200, weight percent. For plywood, it is preferred to range from 0.5 to 200, particularly 10 to 150, weight percent.

In the present invention, the "solvent" which dissolves the isocyanate compound or polymer, is a liquid at room temperature, and both solubilities, that of "solvent" in water and of water in "solvent" is preferably below 5 weight percent at a temperature between 20 to 30°C.

As the "solvent", typical examples are, aliphatic or aromatic hydrocarbons, or mixtures thereof as the main component (such as toluene, xylene, benzene, gasoline, kerosene, ligroin, tetrahydronaphthalene, decahydronaphthalene, turpentine oil, pine oil, liquid paraffin and alkylbenzenes), halogenated hydrocarbons (such as methylene chloride, chlorobenzene, chlorotoluene and bromobenzene), ketones (such as methyl isobutyl ketone, methyl *n*-amyl ketone, methyl *n*-hexyl ketone, ethyl *n*-butyl ketone, di-*n*-propyl ketone and acetophenone), ethers (such as, isopropyl ether, methylphenyl ether, ethylbenzyl ether and furan), lower aliphatic esters (such as acetic acid isopropyl ester, acetic acid butyl ester, and propionic acid butyl ester, etc.), phthalic acid esters (such as, phthalic acid butyl ester, phthalic acid dioctyl ester and phthalic acid butyl-benzyl ester), oleic acid esters, adipic

acid esters, azelaic acid esters, sebacic acid esters, stearic acid esters, benzoic acid esters, abietic acid esters, oxalic acid esters and phosphoric acid esters. And oils composed mainly from higher aliphatic acid esters such as castor oil, are also available.

If the "solvent" has an active hydrogen as a carboxy-, hydroxy- or amino-group in the molecule, upon mixing with the isocyanate compound or polymer, it reacts easily, resulting in a decrease in water resistance. Dilute isocyanate solutions prepared from active hydrogen solvents are ineffective in the present invention. On the other hand, in cases where the "solvent" has no active hydrogen, it is possible to reduce the concentration of isocyanate compound or polymer in the solution to the lowest limit at which the isocyanate solution can still be dispersed uniformly in water. Considering the waterproof effect and dispersion effect, it is desirable to dissolve the isocyanate compound or polymer in an amount of solvent ranging from 10 to 400 weight percent or more, and most desirably 50 to 300 weight percent.

As the boiling point of the "solvent" can vary, it is also desirable to select a solvent that matches the present process and use conditions.

For example, when the composition of the present invention is used as an adhesive for plywood, it is advisable to use nonvolatile solvents having boiling points higher than 200°C., such as dibutyl phthalate, dioctyl phthalate or oleic acid methyl ester, to avoid odour, since the thermal press cycle for adhesion is carried out under ambient conditions. In this case, those solvents remain in the layer of adhesive, acting as a plasticizer. If, however, it is undesirable to have "solvent" remain in the layer of adhesive, a solvent of low boiling point should be used.

The effect of the "solvent" in the adhesive is to disperse the isocyanate uniformly in an aqueous solution, emulsion or latex containing PVA, vinyl acetate polymer or butadiene polymer, and to protect the isocyanate groups from direct contact with the water molecules in an emulsion.

In order to get an adhesive as a uniform dispersion, it is better to agitate it rather strongly during the addition of the solution of isocyanate compound or polymer in the "solvent", to the aqueous solution or emulsion or latex.

It is preferable to add an anionic surfactant to an adhesive mixture in accordance with the present invention. In the case, the PVA aqueous solution may also contain the above mentioned emulsion or latex. By adding an anionic surfactant, enhancement of water resistance, lessening of change in water resistance with time, reduction of bubble-formation, stabilization of the viscosity of the adhesive solution, and furthermore, preparation of an

emulsified solution are easily obtained. The useful life of the adhesive can be increased markedly with the method of the present invention.

Anionic surfactants are most suitable for the present purpose. Cationic, nonionic or amphoteric surfactants show relatively poor effectiveness as compared with an anionic surfactant. A cationic surfactant has an accelerating effect on the rate of reaction, which increases the bubble-forming tendency of the mixture resulting in poor stability of the final product. Any type of anionic surfactant can be used for the process of the present invention, irrespective of the chemical structure of the surfactant. The anionic surfactants used in the practice of the present invention are, for instance, carboxylic acid salts such as soaps from aliphatic acid salts; sulfuric acid ester salts such as salts of sulfuric acid esters of higher alcohols (e.g. sodium lauryl sulfate), sulfonic oils (e.g. Turkey red oil), sulfuric fatty acid esters (e.g. sodium dioctyl sulphosuccinate) and sulfuric olefins (e.g. sodium alkylbenzene sulfonates); sulfonic acid salts such as alkyl benzene sulfonic acid salts, alkyl naphthalene sulfonic acid salts, alkyl sulfonic acid salts, Igepon T, Aerosol OT, and lignin sulfonic acid salts; and phosphonic ester salts such as phosphonic acid esters of higher fatty acids.

The concentration of the surfactant can range from 1 to 10 weight percent, preferably from 2 to 4 weight percent, based on the weight of ingredients (1) and (2). When it is used in amounts less than 1 weight percent, the effect of the surfactant is not obtained. When it is used in large amounts exceeding 10 weight percent, the surfactant gives undesired effects such as coagulation of the emulsion. The reason why addition of anionic surfactant imparts improved stability to the admixture of the present invention is not well understood. It is currently believed (but this is not to be taken as a binding explanation) that in the present process, surfactant molecules are absorbed on the surface of the emulsified particles to prevent isocyanate molecules from coming into direct contact with water molecules. Thus, de-composition of the isocyanate is retarded to impart increased stability to the emulsified solution.

Furthermore, the adhesives of the present invention can contain other additives. The effect of the additives is not only to increase the amount of adhesion, but also to increase the waterproof property and initial adhesive power, by reacting with the other components of the adhesive, especially with the polyisocyanate.

Such additives include wheat flour, starches, extracted soybean powder, blood powder and other additives such as used in urea resins. Among these additives, flour and starches are preferred, as they enhance the water resistance

by reacting with isocyanate, and, moreover, although they are not like an adhesive paste in a cold water, they are converted to such a state by heating during the operation for adhesion.

Furthermore, the adhesives of the present invention can contain fillers. The effect of fillers is not only to prevent excessive penetration of adhesive into the wood, but also to impart better water resistance and initial adhesive strength by reacting with the isocyanate.

Suitable fillers include organic substances such as wood powder and powder of walnut shell, as well as inorganic substances, such as clay, kaolin and talc.

Though the mixing ratio of additive or filler depends upon the ultimate end use, the amount of additive or filler is usually in the range of 10 to 100 weight percent based on the weight of ingredients (1) and (2). The amount is preferably 15 to 50 weight percent when the adhesive is to be used for plywood. These additives and fillers may be used individually or in any mixture thereof. It is most desirable to combine the additives and fillers.

Furthermore, the adhesive of the present invention can be admixed with an accelerator such as boric acid, aluminum sulfate, alum or chromium borate, and/or a viscosity increasing agent such as hydroxyethyl cellulose, carboxymethyl cellulose, methylcellulose or salts of polyacrylic acid.

Further, the adhesive of the present invention can additionally include a material such as waterglass (an aqueous solution of sodium or potassium tetrasilicate) to delay the drying of the adhesive.

Moreover, the adhesive of the present invention can also contain a formalin type of thermosetting resin, e.g., urea and/or melamine-formalin resin.

Although sufficient strength of adhesion can

be achieved by cold pressing of the adhesive, it is desirable to use a hot press treatment to get better water resistance and adhesion.

Although the main purpose of the adhesives of the present invention is for manufacturing plywood or manufacturing with plywood, they are also useful for other woodwork, manufacture of particle board or corrugated cardboard and for promoting adhesion of materials such as metallic foil, paper and fibers.

The following examples further define and explain the present invention. It is to be understood, however, that the invention is not limited to these examples. Unless otherwise stated, all percentages and parts are by weight.

#### Examples 1—4.

Four kinds of adhesive with different kinds of solvent were prepared. Those solvents were dioctyl phthalate, dibutyl phthalate, toluene and methylene chloride. "Millionate MR", an isocyanate belonging to the MDI series produced by Nippon Urethane Incorp., was initially diluted with these solvents to form 50% solutions. Then, each solution was added, under sufficient agitation, to a 10% aqueous solution of "PVA-117", polyvinyl alcohol with a degree of polymerization of 1,750 and 98.5 mole % degree of saponification, produced by Kararay Co., Ltd., in the amount of 200 percent based on the solids content of PVA, and then, 200% of clay based on the solids content of PVA was added.

Using these four adhesives, plywood was prepared from three single boards of lauan, 0.7mm, 1.4mm and 0.7mm in thickness, under the following conditions:

Amount of adhesive used: 30g/0.09183m<sup>2</sup>

Cold press: 10 kg/cm<sup>2</sup> for 20 min.

Hot press: 10 kg/cm<sup>2</sup> for 1 min. at 120°C.

The resulting adhesive strengths in tepid water are summarized in Table I:

TABLE I

Example No.	Solvent	B.P. of solvent	Solubility of solvent in water	Solubility of water in solvent	Adhesive strength in tepid water	Wood break (%)
1	dioctyl phthalate	340°C.	0.02 wt. %	1.00 wt. %, 20°C.	10.2 kg/cm <sup>2</sup>	6
2	dibutyl phthalate	339°C.	0.01 wt. %, 20°C.	0.46 wt. %, 20°C.	12.3 kg/cm <sup>2</sup>	30
3	toluene	110.6°C.	0.047 wt. %, 16°C.	0.15 mol %, 10°C.	14.0 kg/cm <sup>2</sup>	27
4	methylenedichloride	40.4°C.	2 wt. %, 20°C.	0.17 wt. %, 25°C.	14.4 kg/cm <sup>2</sup>	34

## Example 5.

10 parts of a mixture of Colonate L, an adduct of tolylenediisocyanate with trimethylol propane, produced by Nippon Urethane Incorp., and dibutyl phthalate in the ratio of one to one, was added, under strong agitation, to 100 parts of an emulsion containing 50 weight percent of copolymer of ethylene and vinyl acetate and 5 weight percent of PVA. Next, 2.5 parts of wood powder sieved through 200 mesh, 2.5 parts of wheat flour, 2.5 parts of clay and 15 parts of water were added to it. The prepared adhesive, after a persistent agitation, was tested as in Example 1.

The observed strength of adhesion of plywood was as follows:

Adhesive strength in a normal state  
15.4 kg/cm<sup>2</sup> wood break (89%), 20  
Adhesive strength in tepid water  
14.2 kg/cm<sup>2</sup> wood break (61%).

Both strengths were above 7 kg/cm<sup>2</sup>, which is the lowest permissible limit.

## Example 6.

In order to test the applicability of the adhesive of the invention to woodworking, the adhesive in Example 2 was examined, by preparing plywood from three single boards of luan, 1mm each in thickness, under the conditions of 22g/ft<sup>2</sup> of adhesive and a cold press at 10 kg/cm<sup>2</sup> for 30 min.

The adhesive strength was observed after aging for one day, as shown in Table II.

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TABLE II

Solvent Used	Adhesive strength in normal state (wood break %)	Adhesive strength in tepid water (wood break %)
dibutyl phthalate	15.1 kg/cm <sup>2</sup> (62)	10.4 kg/cm <sup>2</sup> (18)

## Comparative Example

At first, 10 weight percent solution of PVA, degree of polymerization of 1700 and a degree of saponification of 98 molar percent, was coated on three single boards, 1 mm each in thickness, and dried by evaporation of water. Then, they were coated again with a 10% solution of hexamethylene diisocyanate in toluene and laminated upon each other, immediately, and pressed at 10 kg/cm<sup>2</sup> of pressure for 10 min. to prepare a plywood. The observed adhesive strength, both at room temperature and in tepid water was too low to obtain a useful plywood product.

## Example 7.

25 grams of polyvinyl alcohol (having a degree of polymerization of 500 and a degree of saponification of 98.7 mole %) was dissolved in 100g of water. 100 g of a styrene-butadiene polymer latex (having a solids content of 48% and comprising 45% of styrene and 55% of butadiene) and 15g of wheat flour were added in succession to the above

solution, and they were well mixed to obtain a white suspension. Then, 16.5g of a trimethylol propanetolylene diisocyanate adduct (45% solution of *Desmodur L* manufactured by Bayer A.G. in ethyl acetate (was added to the suspension and they were well mixed to disperse the adduct in the suspension. The resulting adhesive composition (about 40 minutes had passed from the addition of the isocyanate compound) was coated on luan veneers (3 veneers each having 1mm thickness; total thickness being 3mm) in an amount of 32g/900cm<sup>2</sup>, and the veneers were lapped and allowed to stand still for 15 minutes. Then, the assembly was subjected to temporary compression (cold press) under a pressure of 10kg/cm<sup>2</sup> for 10 minutes, and the hot press was conducted at 120°C under a pressure of 10kg/cm<sup>2</sup> for 1 minute. Results of the bonding strength test made accordingly to JAS (Japanese Agricultural Standard) (Notification No. 383 of the Ministry of the Agriculture and Forestry) are shown in Table III.

TABLE III

	Bonding Strength (kg/cm <sup>2</sup> )		
	Maximum	Minimum	Average
Normal State Bonding Strength	24.6	19.8	22.1
Bonding Strength after Warm and Cold Water Treatment	16.4	12.0	14.7
Note: the value of the bonding strength was determined by conducting the measurement on 15 test pieces.			

The initial bonding strength (temporary bonding strength) was quite excellent and no partial peeling was observed.

## Example 8.

500 g of a carboxyl-group-containing styrene-butadiene latex (composed of 52% by weight of styrene and 48% by weight of butadiene; carboxyl group content of 40 millimoles per 100 g solid; solid content of 50%) was incorporated in succession with 167g of a separately prepared aqueous solution of polyvinyl alcohol (having a degree of polymerization of 1700 and a degree of saponification of

87 mole %; PVA concentration of 15% by weight), 50 g of clay produced by Shokozan and 27 g of water, and the mixture was well blended. The resulting solution was admixed with 10 grams of triphenylmethane triisocyanate (60% solution of *Desmodur R* manufactured by Bayer A. G. in ethyl acetate), and they were well mixed under agitation to form an adhesive composition according to this invention.

In the same manner as described in Example 1, a plywood was prepared and the bonding strength was tested to obtain results shown in Table IV.

TABLE IV

	Bonding Strength (kg/cm <sup>2</sup> )		
	Maximum	Minimum	Average
Normal state bonding strength	20.6	17.2	18.9
Bonding strength after warm and cold water treatment	15.0	12.5	13.4

Note: the value of the bonding strength was determined by conducting the measurement on 10 test pieces.

#### Example 9.

25 g of polyvinyl alcohol (having a degree of polymerization of 400 and a degree of saponification of 87 mole %) was dissolved under heat in 100 g of water, and 35 g of a styrene-butadiene latex (styrene/butadiene weight ratio of 35/65; carboxyl group content of 20 millimoles per 100 g solid; solid content of 50%) and 25 g of gypsum powder (passable through a 25-mesh sieve) were added in succession to the above solution. The mixture was well blended and the resulting solution was incorporated with 22 g of a trimethylol propane-tolylene diisocyanate adduct (45% solution in ethyl acetate). The mixture was well agitated to form an adhesive composition.

In the same manner as described in Example 1, a plywood was prepared with use of the so obtained adhesive composition, and test pieces were immersed in water maintained at 25°C. for 20 days, and then, they were dried in a desiccator maintained at 40°C. for 24 hours. With respect to the so treated test species, the normal state bonding strength and the bonding strength after warm and cold water treatment were determined according to the JAS method referred to in Example 7. As a result, it was found that the normal state bonding strength was 16.4 kg/cm<sup>2</sup> and the bonding strength after warm and cold water treatment was 10.2 kg/cm<sup>2</sup>.

#### Example 10.

25 g of polyvinyl alcohol (having a degree of polymerization of 700 and a degree of saponification of 99 mole %) was dissolved with heat in 100 g of water, and 60 g of styrene/butadiene latex (styrene/butadiene weight ratio of 65/35; carboxyl group content of 70 millimoles per 100 g solid; solid content of 50%), 40 g of wood flour (cryptomeria flour passable through a 150-mesh sieve) and 15 g of water were added to the above solution and mixed therewith sufficiently to form a dispersion. The resulting dispersion

was incorporated with 12.5 g of an isocyanate polymer ("Millionate MR" manufactured by Nippon Polyurethane; 40% solution in toluene), and the mixture was blended and agitated sufficiently to obtain an adhesive composition of this invention.

In the same manner as described in Example 12, a plywood was prepared and the bonding strength was determined to obtain the following results:

#### Bonding Strength

Normal state bonding strength (average value of 10 test pieces):

bonding strength of 19.3 kg/cm<sup>2</sup> with a wood portion break ratio of 94%.

Bonding strength after warm and cold water treatment (average value of 10 test pieces):

bonding strength of 13.6 kg/cm<sup>2</sup> with a wood portion break ratio of 23%.

In the case of test pieces of a plywood formed with use of an adhesive free of the isocyanate compound, all the test pieces were peeled by the warm and cold water treatment.

#### Example 11.

Three parts of PVA were dissolved in water on heating, 0.2 part of "Nissan Rapizol B-30" (an anionic surfactant made by Nippon Oils and Fats Co., Ltd., sodium dioctyl sulfosuccinate) was added to the aqueous solution, mixed well, and 15 parts of the dioctyl phthalate solution of 75% isocyanate ("Millionate MR" made by Nippon Polyurethane Co., Ltd.) under stirring for 5 minutes to yield an emulsified solution. Films were prepared from the resulting emulsion in different periods of 0, 3, and 10 hours at 20°C., after preparation of the emulsion. The water resistance of the films (solubility of the film in water) were measured. The results are shown in Table V.

TABLE V

Standing time of emulsion (hr)	0	3	10
Solubility of Film in water	1.7%	2.4%	2.5%



Condition of film-preparation: 120°C., 1 min., by hot pressing  
 Condition of film-dissolving: boiled with water at 100°C. for 2 hours

Features of viscosity change of the emulsion and the amount of bubbles formed in the emulsion at different times are shown in Table VI.

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TABLE VI

	Viscosity (CPS, 20°C.)		Amount of bubbles (10 hrs) (% amount of the emulsion)
	20 min.	4 hrs.	
With "Nissan Rapizol B-30"	4,500	5,300	5

- 10 From the Table it can be seen that the emulsion containing "Nissan Rapizol B-30" exhibited a very small increase in viscosity and a small amount of bubble-formation.

except adding different types of surfactants. Changes in water resistance of the resulting films, viscosity of the emulsions, and bubble-formation from the emulsion with time were measured. As shown in Table VII, anionic surfactants remarkably improve the above properties of the films and the emulsions.

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## Example 12.

- 15 The procedure of Example 1 was repeated

TABLE VII

	Surfactant	Solubility of film (%)		Viscosity (CPS, 20°C.)		Amount of bubbling at 10 hrs.)
		0hrs.	10hrs.	20min.	4hrs	
Examples of the present invention	Nissan Rapizol B-30 <sup>(1)</sup>	2.4	2.5	3,500	3,800	8
	Nissan Sintorex <sup>(2)</sup>	2.5	2.9	4,200	10,500	5
	Nissan Newrex Powder W <sup>(3)</sup>	3.3	4.7	3,800	8,500	25
Comparative Examples	Nissan Kation BB <sup>(4)</sup>	4.2	18.5	7,300	>100,000	>200
	Nissan Kation M <sub>2</sub> -100 <sup>(5)</sup>	6.4	19.1	16,400	26,000	>200
	Nissan Nonion L-4 <sup>(6)</sup>	4.1	17.2	4,300	29,000	180

(<sup>1</sup>): Nissan Rapizol B-80", Anionic surfactant of Nippon Oils and Fatts Co., Ltd., Sodium dioctyl sulfo succinate.

(<sup>2</sup>): "Nissan Sintorex", Anionic surfactant of Nissan Oils and Fatts Co. Ltd., Sodium salt of sperm alcohol sulfuric ester.

(<sup>3</sup>): "Nissan Newrex Powder W", Anionic surfactant of Nippon Oils and Fatts Co. Ltd., Sodium dodecyl benzene sulfate.

(<sup>4</sup>): "Nissan Kation BB", Cationic surfactant of Nippon Oils and Fatts Co. Ltd., Dodecyl trimethyl ammonium chloride.

(<sup>5</sup>): "Nissan Kation M<sub>2</sub>-100", Cationic surfactant of Nippon Oils and Fatts Co. Ltd., Hexadecyl dimethyl benzyl ammonium chloride.

(<sup>6</sup>): "Nissan Nonion L-4", Nonionic surfactant of Nippon Oils and Fatts Co. Ltd., Polyoxy ethylene monolaurate.

## Example 13.

To 100 parts of an aqueous solution of 10% PVA (degree of polymerization 1700, degree of saponification 98 mole %) were added 15 parts of dioctyl phthalate solution of 70% isocyanate (Nippon Polyurethane "Millionate MR") and 20 parts of "Tsuchiya clay" and further added "Rapizol B-30" at

0.2 weight percent, based on the weight of the total mixture mixed well.

Adhesive tests were carried out on a piece of plywood 3 mm thick (composed with 3 plates each being 1 mm thick) under the conditions set forth below. The conditions and the results obtained are shown in Table VIII.

TABLE VIII

	Viscosity CPS (30°C)		Adhesion strength <sup>(1)</sup>	
	0 <sup>(2)</sup>	6 hrs <sup>(2)</sup>	0 <sup>(2)</sup>	6 hrs <sup>(2)</sup>
			kg/cm <sup>2</sup>	kg/cm <sup>2</sup>
With "Nissan Rapizol B-30"	4,900	5,100	13.3	13.0

<sup>(1)</sup> Adhesion strength in hot or cold water.

<sup>(2)</sup> Time after preparation of the adhesive emulsion.

Amount of adhesive coating : 30g/30×30cm<sup>2</sup>

Hot pressing : temperature 120°C., time 60 sec.

## WHAT WE CLAIM IS:—

1. An adhesive composition comprising (1) an aqueous solution of poly vinyl alcohol and (2) a hydrophobic solution of an isocyanate compound or polymer that contains two or more isocyanate groups to the molecule.

2. An adhesive composition as claimed in Claim 1 that also contains an anionic surface-active agent.

3. An adhesive composition as claimed in Claim 1 or 2 that also contains an aqueous emulsion of vinyl acetate polymer.

4. An adhesive composition as claimed in Claim 1 or 2 that also contains an aqueous latex of butadiene polymer.

5. An adhesive composition as claimed in Claim 1 that also contains both an aqueous emulsion of vinyl acetate polymer and an aqueous latex of butadiene polymer.

6. An adhesive composition as claimed in Claim 5 that also contains an anionic surface-active agent.

7. An adhesive composition as claimed in Claim 3, 5 or 6, in which the aqueous emulsion of vinyl acetate polymer is an aqueous emulsion of polyvinyl acetate, an aqueous emulsion of a copolymer of vinyl acetate and ethylene or an aqueous emulsion of a copolymer of vinyl acetate and another comonomer polymerizable with vinyl acetate.

8. An adhesive composition as claimed in Claim 4, 5 or 6, in which the aqueous latex of butadiene polymer is an aqueous latex of a copolymer of styrene and butadiene or an aqueous latex of a copolymer of acrylonitrile and butadiene.

9. An adhesive composition as claimed in any preceding claim that also contains a viscosity-increasing agent.

10. An adhesive composition as claimed in Claim 9, in which the viscosity-increasing agent is hydroxyethyl cellulose, carboxymethyl cellulose, methyl-cellulose or a salt of polyacrylic acid.

11. An adhesive composition as claimed in any preceding claim additionally including waterglass.

12. An adhesive composition as claimed in any preceding claim additionally including a formalin-type thermosetting resin.

13. An adhesive composition as claimed in Claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

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